

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平6-149142

(43)公開日 平成6年(1994)5月27日

(51)Int.Cl. ⁵	識別記号	序内整理番号	F I	技術表示箇所
G 0 3 H 1/02		8105-2K		
G 0 2 B 1/10		Z 7132-2K		

審査請求 未請求 請求項の数 1 (全 10 頁)

(21)出願番号	特願平4-328636	(71)出願人	000222118 東洋インキ製造株式会社 東京都中央区京橋2丁目3番13号
(22)出願日	平成4年(1992)11月13日	(72)発明者	山口 岳男 東京都中央区京橋2丁目3番13号東洋インキ製造株式会社内
		(72)発明者	島羽 泰正 東京都中央区京橋2丁目3番13号東洋インキ製造株式会社内
		(72)発明者	安池 円 東京都中央区京橋2丁目3番13号東洋インキ製造株式会社内

(54)【発明の名称】 体積位相型ホログラムの製造方法

(57)【要約】 (修正有)

【目的】化学的安定性や耐環境特性に優れた高性能の体積位相型ホログラムを製造する。

【構成】1) アクリル酸エステルまたはメタクリル酸エステルの単重合体、またはこれらのモノマーとビニールモノマーとの共重合体の高分子化合物、2) 重合可能なエチレン性不飽和結合を有する化合物、3) 3-ケトクマリン類、および4) ジアリールヨードニウム塩、の4成分の組合せを含むホログラム記録用感光材料を光学的に透明な基材と保護膜とで挟んだ感光膜をホログラム記録媒体として干渉パターンで露光するが、露光の前か後に紫外線、可視光線、電子線などの活性線で付加的な露光を与えるか、または加熱処理する第1の工程、溶媒で記録媒体を膨潤させる第2の工程、さらに記録媒体を溶解性及び膨潤性に乏しい溶媒に接触させ収縮させる第3の工程により体積位相型ホログラムを製造する。

(2)

特開平6-149142

1

【特許請求の範囲】

【請求項】 アクリル酸エステルまたはメタクリル酸エステルの単重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)、3-ケトクマリン類(C)およびシアリールヨードニウム塩(D)との組合せを含むことを特徴とするホログラム記録用感光材料が、光学的に透明な基材と光学的に透明な保護膜に挟まれて感光膜を形成していることを特徴とするホログラム記録媒体を用いて体積位相型ホログラムを製造するに当たって、該ホログラム記録媒体を照射線の干渉パターンに露出する第1の工程、該記録媒体を膨潤せしめる溶媒にて処理する第2の工程、さらに該記録媒体を膨潤性に乏しい溶媒に接触させ収縮せしめる第3の工程からなる工程と、該記録媒体を第1の工程の前あるいは後に、紫外線、可視光線、電子線などの活性線への露出、(および)または加熱によって処理せしめる工程とを具備してなることを特徴とする体積位相型ホログラムの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、化学的安定性や耐環境特性に優れ、且つ感度特性、解像度、回折効率及び透明性に特に優れた体積位相型ホログラムの製造方法に関するものである。

【0002】

【従来の技術】 従来、ホログラム記録媒体として、漂白処理銀塩および重クロム酸ゼラチン系の感光材料が一般に使用されてきた。しかし、これらのホログラム記録媒体によるホログラムの製造は、何れも感光板の作製方法、ホログラム製造のための処理が煩雑であったり、製造されたホログラムが耐環境特性、例えば耐湿性、耐候性に劣る、また解像度に限界があるという問題点を有していた。

【0003】 かかる問題を解決するために、耐環境特性に優れ、且つ高解像度、高回折効率などのホログラムの有すべき特性を備えた体積位相型ホログラムの製造方法として、フォトポリマーを利用した例が知られている。例えば、特公昭62-22152号公報では、担体となるべき重合体中に光重合性物質である2個以上のエチレン性不飽和結合を有する多官能単量体を分散せしめた感材を、照射線の干渉パターンに露出する第1の工程、該感材を第1の溶媒で処理し該感材を膨潤せしめる第2の工程、膨潤作用の乏しい第2の溶媒で処理し該感材を収縮せしめる第3の工程とを具備してなることを特徴とするホログラム製造方法が開示されている。しかしながら、該公知文献における方法においては、第2の現像工程において、照射線の干渉パターンに露出されなかった部位、いわゆる未露光部位において著しく白化するとい

2

う問題点があった。また、該公知文献に記載の感材を用いて、充分な回折効率を有するホログラムを製造するためには50mJ/cm²以上の露光エネルギーが必要とされ、ホログラムの大規模製、即ち露光時間の短縮化において重要な特性となる感度特性をより一層向上させることが望まれた。

【0004】 一方、3-ケトクマリン誘導体とシアリールヨードニウム塩との組合せから成る光重合開始剤が、特開昭60-88005(特公平3-62162号公報)にて提案され開示されているが、当該公知文献においてはホログラム記録のための具体的な例示あるいは作成法に関する記載もされておらず、当該公知文献記載の光重合開始剤の単なる利用では体積位相型ホログラムを作成することはできなかった。

【0005】 また、特願平4-31590号公報においては、ポリメタクリル酸メチル、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物、3-ケトクマリン類およびシアリールヨードニウム塩との組合せからなることを特徴とするホログラム記録用感光材料が提案されているが、現像処理工程において、未露光部位が著しく白化するという問題点があった。

【0006】 また、高分子化合物、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物および3-ケトクマリン類およびラジカル発生剤とを構成成分とするホログラム記録用感光材料及びそれを用いたホログラムの製造方法がいくつか提案されている。例えば、特開平2-216180号公報には、ポリビニルカルバゾールあるいはその誘導体、多官能モノマー、クマリン誘導体及び有機過酸化物からなるホログラム記録用組成物が、また特開平4-13172号公報には、ポリビニルカルバゾール、メタクリレート系化合物、ケトクマリン色素及び鉄アレーン錯体からなるホログラム記録用組成物が開示されている。これらのホログラム記録用感光材料は、ポリビニルカルバゾールあるいはその誘導体を主剤としているため、化学的に安定でかつ高い解像度、耐湿性、耐熱性、耐候性を有しているものの、ポリビニルカルバゾールは、該現像処理工程において結晶化して白化しやすく、透明性の再現性が悪いという問題点や、ポリビニルカルバゾールの剛直性のために、感度特性において劣るという欠点があった。一方、特開平2-216181号公報においては、ポリビニルピロリドン、多官能モノマー、クマリン色素及び有機過酸化物とからなるホログラム記録用組成物が開示されているが、該公知材料は、高分子化合物が水膨潤性あるいは水溶性であるために、耐湿性や耐水性などの耐環境特性に劣るという欠点を有していた。

【0007】

【発明が解決しようとする課題】 本発明は、化学的安定性や耐環境特性に優れ、且つ感度特性、解像度、回折効率及び透明性に特に優れた体積位相型ホログラムの製造

(3)

特開平6-149142

3

方法を提供するものである。

【0008】

【課題を解決するための手段】本発明者らは、以上の諸点を考慮し、上記目的を達成すべく鋭意検討した結果、本発明に至ったものである。すなわち、本発明は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)、3-ケトクマリン類(C)およびシアリールヨードニウム塩(D)を含むことを特徴とするホログラム記録用感光材料が、光学的に透明な基材と光学的に透明な保護膜に挟まれて感光膜を形成していることを特徴とするホログラム記録媒体を用いて体積位相型ホログラムを製造するに当たって、該ホログラム記録媒体を放射線の干渉パターンに露出する第1の工程、該記録媒体を膨潤せしめる溶媒にて処理する第2の工程、さらに該記録媒体を膨潤性に乏しい溶媒に接触させ収縮せしめる第3の工程とからなる工程と、該記録媒体を第1の工程の前あるいは後に、紫外線、可視光線、電子線などの活性線への露出、(および)または加熱によって処理せしめる工程とを具備してなることを特徴とする体積位相型ホログラムの製造方法である。

【0009】以下、詳細にわたって本発明を説明する。

【0010】本発明のホログラム記録媒体において使用される高分子化合物(A)は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルと、その他のビニルモノマーとの2成分以上の共重合体である。具体的なアクリル酸エステルまたはメタクリル酸エステルの単一重合体としては、メチル、エチル、プロピル、イソブチル、n-ブチル、sec-ブチル、tert-ブチル、ペンチル、ネオペンチル、ヘキシル、ヘプチル、オクチル、ノニル、ドデシル、2-メチルブチル、3-メチルブチル、2-エチルブチル、1,3-ジメチルブチル、2-エチルヘキシル、2-メチルペンチル、シクロヘキシル、アダマンチル、イソボルニル、ジシクロペンタニル、テトラヒドロフルフリールなどの鎖状、分枝状及び環状アルキルのアクリル酸またはメタクリル酸エステルモノマーの重合体、フェニル、4-メトキシカルボニルフェニル、4-エトキシカルボニルフェニル、4-ブトキシカルボニルフェニル、4-tert-ブチルフェニル、ベンジル、4-フェニルエチル、4-フェノキシジエチレングリコール、4-フェノキシテトラエチレングリコール、4-フェノキシヘキサエチレングリコール、4-ビフェニルなどの芳香環を含有するアクリル酸またはメタクリル酸エステルモノマーの重合体、フェロセニルメチル、フェロセニルエチルなどの鉄原子を含有するアクリル酸またはメタクリル酸エステルモノマー

4

の重合体、トリフルオロエチル、テトラフルオロプロピル、ヘプタデカフルオロデシル、オクタフルオロベンチル、2,3-ジブロモプロピルなどのハロゲン原子を含有するアクリル酸またはメタクリル酸エステルモノマーの重合体、トリメトキシシリルプロピルなどのケイ素原子を含有するアクリル酸またはメタクリル酸エステルの重合体、グリシジルアクリレートやグリシジルメタクリレートなどのエポキシ基を含有するアクリル酸またはメタクリル酸エステルモノマーの重合体、N,N-ジメチルアミノエチル、N,N-ジエチルアミノエチル、1-ブチルアミノエチルなどのアミノ基を含有するアクリル酸またはメタクリル酸エステルモノマーの重合体などが挙げられる。これらのアクリル酸エステルまたはメタクリル酸エステルモノマーは、必要に応じて2成分以上の共重合体として使用することが可能である。

【0011】前記したアクリル酸エステルまたはメタクリル酸エステルモノマーとの2成分以上の共重合体として使用できるビニルモノマーとしては、ブタジエン、イソプレン、アクリルアミド、N-ブチルアクリルアミド、N,N-ジメチルアクリルアミド、アクリロニトリル、スチレン、4-プロモスチレン、パーフルオロスチレン、 α -メチルスチレン、ビニルトルエン、酢酸ビニル、塩化ビニル、塩化ビニリデン、N-ビニルピロリドン、N-ビニルカルバゾール、ビニルピリジン、ビニルピロリジンなどが挙げられる。

【0012】本発明のホログラム記録媒体に供される重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)としては、1官能であるビニルモノマーの他にオリゴマーを含むものであり、さらには高分子重合化合物であってもよく、またこれらの混合物であってもよい。その様な化合物としては、アクリル酸、メタクリル酸、イタコン酸、マレイン酸、アクリルアミド、メタクリルアミド、シアセトンアクリルアミド、2-ヒドロキシエチル(メタ)アクリレート、N-ビニルカルバゾール等の高沸点ビニルモノマー、さらには、脂肪族ポリヒドロキシ化合物、例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、テトラエチレングリコール、ネオペンチルグリコール、1,3-プロパンジオール、1,4-ブタンジオール、1,5-ペンタンジオール、1,6-ヘキサンジオール、1,10-デカンジオール、トリメチロールプロパン、ペンタエリスリトール、ジペンタエリスリトール、ソルビトール、マンニトールなどのジあるいはポリ(メタ)アクリルエステル類、芳香族ポリヒドロキシ化合物、例えば、ヒドロキノン、レゾルシン、カチコール、ピロガロール等のジあるいはポリ(メタ)アクリルエステル、イソシアヌル酸のエチレンオキシド変性(メタ)アクリレート、さらには、側鎖にヒドロキシ基やハロゲン化メチル基の如き反応活性を有する官能基を持つ重合体とアクリル酸、メタクリル酸、クロトン酸などの不飽和カルボ

(4)

特開平6-149142

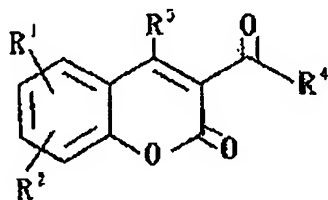
5

ン酸との高分子反応によって得られるポリマーも好適に使用しうる。このような高分子化合物としては、ポリビニルアルコール、ビニルアルコールと酢酸ビニルとの共重合体、ポリエピクロロヒドリン、フェノキシ樹脂、ポリクロロメチルスチレン、2-ヒドロキシ(メタ)アクリレートと種々アクリレートモノマーとの共重合体、フェノール樹脂などが挙げられる。さらには、(メタ)アクリル化されたエポキシ樹脂、ポリエステルアクリレートオリゴマー、(メタ)アクリル化ウレタンオリゴマー、アクロレイン化ポリビニルアルコール等をあげること

【0013】本発明で使用する3-ケトクマリン類(C)としては、一般式(1)

【0014】一般式(1)

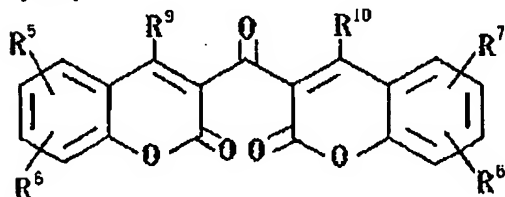
【化1】



【0015】(式中、R¹、R²は、水素原子、ハロゲン原子、アルコキシ基またはジアルキルアミノ基、アリール基あるいは縮合されたベンゼン環を示し、R³は水素原子あるいはシアノ基を示し、R⁴は低級アルキル基、アリール基、複素環、スチリル基を示す)で表わされる3-ケトクマリン類または、一般式(2)

【0016】一般式(2)

【化2】



【0017】(式中、R⁵、R⁶、R⁷、R⁸は、水素原子、ハロゲン原子、アルコキシ基またはジアルキルアミノ基、アリール基あるいは縮合されたベンゼン環を示し、R⁹、R¹⁰は水素原子あるいはシアノ基を示す)で表わされる3位にカルボニル置換されたビスケトクマリン類から選ばれた少なくとも1種の化合物であり、クマリンのベンゼン核にアルコキシ基またはジアルキルアミノ基が置換されていることが望ましい。

【0018】一般式(1)におけるR¹、R²、および一般式(2)におけるR⁵、R⁶、R⁷、R⁸において、ハロゲン原子としてはフッ素、塩素、臭素、ヨウ素原子が、アルコキシ基としては、メトキシ基、エトキシ基、プロポキシ基、イソプロポキシ基、ブトキシ基、ブ

トキシ基、イソブトキシ基、sec-ブトキシ基、tert-ブトキシ基、ベンジルオキシ基などが、ジアルキルアミノ基としてはジメチルアミノ基、ジエチルアミノ基、ジブチルアミノ基などが、アリール基としてはフェニル基、p-トリル基、キシリル基、クメニル基、ナフチル基、アンズリル基、フェナントリル基などが、縮合ベンゼン環としてはナフタレン環、アントラセン環などが挙げられる。また、一般式(1)におけるR⁴において、低級アルキル基としては、メチル基、エチル基、プロピル基などが、アリール基としてはフェニル基、p-トリル基、キシリル基、クメニル基、ナフチル基、アンズリル基、フェナントリル基などが、複素環としてはベンゾフラン環、ベンゾチオフェン環、イソインドール環などが、スチリル基としては、スチリル基、p-ジメチルアミノスチリル基、p-ジエチルアミノスチリル基、p-メトキシスチリル基などが挙げられる。

【0019】一般式(1)で表わされる具体的な化合物の例としては、3-チエノイルクマリン、3-(4-メトキシベンゾイル)クマリン、3-ベンゾイルクマリン、3-(4-シアノベンゾイル)クマリン、3-チエノイル-7-メトキシクマリン、7-メトキシ-3-(4-メトキシベンゾイル)クマリン、3-ベンゾイル-7-メトキシクマリン、3-(4-シアノベンゾイル)-7-メトキシクマリン、5,7-ジメトキシ-3-チエノイルクマリン、5,7-ジメトキシ-3-(4-メトキシベンゾイル)クマリン、3-ベンゾイル-5,7-ジメトキシクマリン、3-(4-シアノベンゾイル)-5,7-ジメトキシクマリン、7-ジエチルアミノ-3-チエノイルクマリン、7-ジエチルアミノ-3-(4-メトキシベンゾイル)クマリン、3-ベンゾイル-7-ジエチルアミノクマリン、7-ジエチルアミノ-3-(4-シアノベンゾイル)クマリン、7-ジエチルアミノ-3-(4-ジメチルアミノベンゾイル)クマリン、3-(2-ベンゾプロイル)-7-ジエチルアミノクマリン、3-シンナモイル-7-ジエチルアミノクマリン、4-シアノ-3-シンナモイル-7-ジエチルアミノクマリン、3-(p-ジエチルアミノシンナモイル)-7-ジエチルアミノクマリン、3-アセチル-7-ジエチルアミノクマリン、3-カルボキシ-7-ジエチルアミノクマリン、3-(4-カルボキシベンゾイル)-7-ジエチルアミノクマリンが挙げられる。また、さらに、クマリンベンゼン環に芳香環が縮合されていてもよい。次に、一般式(2)で表わされる具体的な化合物としては、3,3'-カルボニルビスクマリン、3,3'-カルボニルビス(7-メトキシクマリン)、5,7-ジメトキシ-3,3'-カルボニルビスクマリン、5,7,7'-トリメトキシ-3,3'-カルボニルビスクマリン、3,3'-カルボニルビス(5,7-ジメトキシクマリン)、3,3'-カルボニルビス(5,7-ジエトキシクマリン)、7-ジエチルアミノ

(5)

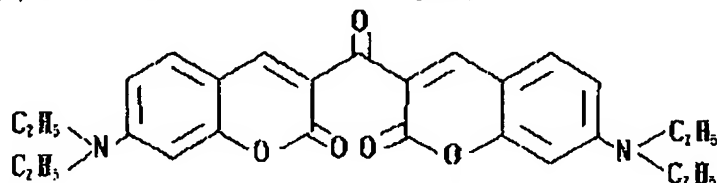
特開平6-149142

7
-3, 3'-カルボニルビスクマリン, 7-ジエチルア
ミノ-5', 7'-ジメトキシ-3, 3'-カルボニル
ビスクマリン, 3, 3'-カルボニルビス(7-ジエチ
ルアミノクマリン), 3, 3'-カルボニルビス(ジ
ロリジノクマリン), 3, 3'-カルボニルビス(4-*

8
*シアノ-7-ジエチルアミノクマリン)等をあげること
ができる。代表的な例として、化合物(a)ないし化
合物(h)を示す。

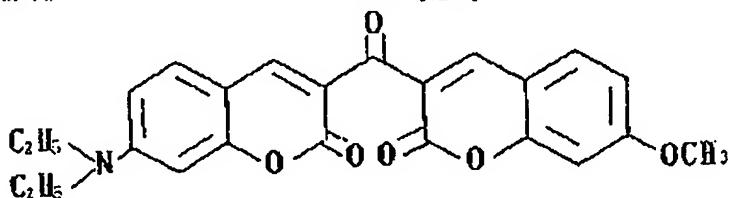
【0020】化合物(a)

【化3】



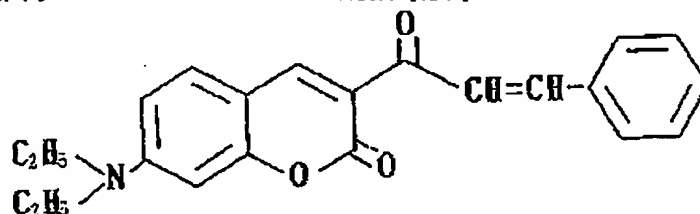
【0021】化合物(b)

※ ※ 【化4】



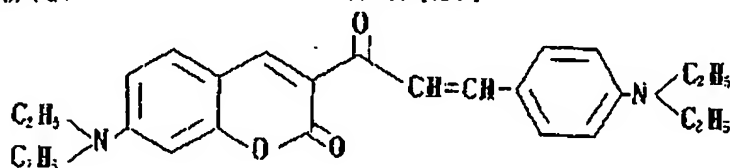
【0022】化合物(c)

★25★ 【化5】



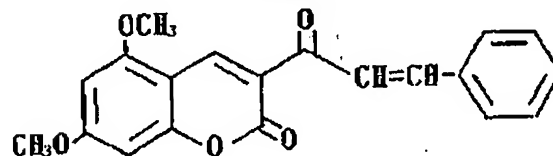
【0023】化合物(d)

☆ ☆ 【化6】



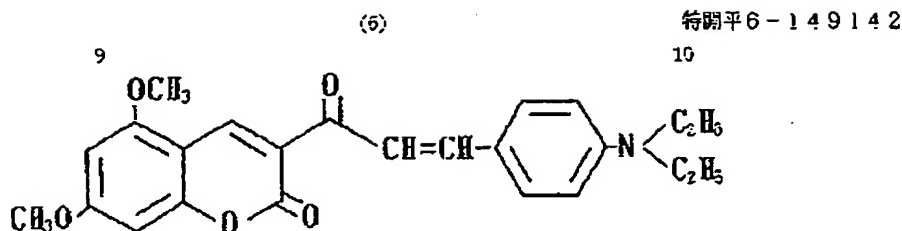
【0024】化合物(e)

◆40◆ 【化7】



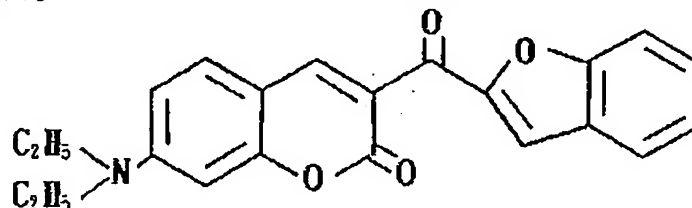
【0025】化合物(f)

【化8】



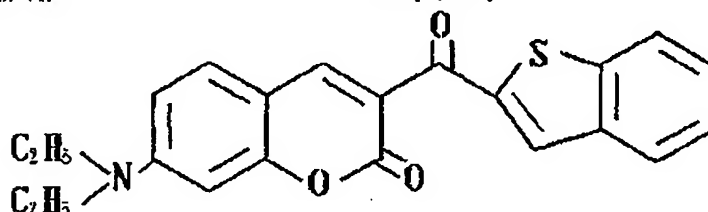
【0026】化合物 (g)

* * 【化9】



【0027】化合物 (h)

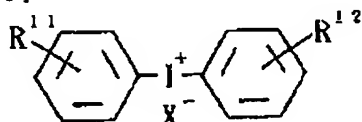
* * 【化10】



【0028】次に、本発明で使用するジアリールヨードニウム塩 (D) は、一般式 (3)

【0029】一般式 (3)

【化11】



(式中、 R^1 、 R^2 は水素原子、低級アルキル基、低級アルコキシ基、シアノ基、ニトロ基またはハロゲン原子を表し、 X^- はハロゲンイオン、 BF_4^- 、 PF_6^- 、 AsF_6^- 、 SbF_6^- 、 ClO_4^- 、 $C_6H_5SO_3^-$ 、 $p-CH_3C_6H_4SO_3^-$ 、 $p-CF_3C_6H_4SO_3^-$ などを示す)で表されるジアリールヨードニウム塩を示す。その様なジアリールヨードニウム塩としては、「マクロモレキュルス (Macromolecules)」、第10巻、第1307ページ (1977年) に記載の化合物、例えば、ジフェニルヨードニウム、ジトリルヨードニウム、フェニル (p-メトキシフェニル) ヨードニウム、ビス (m-ニトロフェニル) ヨードニウム、ビス (p-tert-ブチルフェニル) ヨードニウム、ビス (p-シアノフェニル) ヨードニウム等のクロリド、ブロミド、四フッ化ホウ素塩、六フッ化ホウ素塩、六フッ化リン塩、六フッ化ヒ素塩、六フッ化アンチモン塩、過塩素酸塩、ベンゼンスルホン酸塩、p-トリエンズルホン酸塩、p-トリフルオロメチルベンゼンスルホン酸塩等が例示される。

【0030】本発明で使用するホログラム記録媒体は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物 (A)、重合可能なエチレン性不飽和結合を少なくとも1個有する化合物 (B)、3-ケトクマリン類 (C) 及びジアリールヨードニウム塩

(D) を適当な溶媒中に溶解させ、得られた溶液を光学的に透明な基板上、あるいは光学的に透明な保護膜上に皮膜状に塗布して形成される。塗布される厚みは、乾燥後の膜厚として1 μm から20 μm にすることが好ましく、4 μm から10 μm の範囲がより好ましい。上記各成分の配合比に特定の制限はないが、照射用レーザー光の透過率が1%以上となるように3-ケトクマリン類

(C) の濃度を調整することが好ましい。さらに必要に応じて、各種添加剤、例えば可塑剤、酸化防止剤、重合禁止剤等を添加してもよい。

【0031】アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物 (A) のホログラム記録材料に占める量は、高回折効率、高解像度、高透明性を有する体積位相型ホログラムを製造するためには、10~90重量%、好ましくは、30~70重量%である。重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物 (B) の使用量は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノ

11

マーとの2成分以上の共重合体である高分子化合物
(A) 100重量部に対し10~200重量部、好ましくは40~150重量部である。上記範囲を逸脱すると高い回折効率の維持および感度特性の向上が困難となるので好ましくない。

【0032】本発明のホログラム記録媒体で使用する光重合開始剤のうち、3-ケトクマリン類(C)は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A) 100重量部に対し、0.1~30重量部、好ましくは、0.5~15重量部の範囲で使用される。使用量は、感光膜厚と、該膜厚の光学密度によって制限を受ける。即ち、光学密度が2を越さない範囲で使用することが好ましい。また、光重合開始剤のもう一方の成分であるジアリールヨードニウム有機ホウ素錯体(D)は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A) 100重量部に対し、0.1~20重量部、好ましくは1~15重量部の範囲で使用される。

【0033】本発明におけるホログラム記録用感光材料は、光学的に透明な基材と光学的に透明な保護膜に挟まれた記録媒体として使用される。光学的に透明な基材としてはガラス板、ポリカーボネート板、ポリメチルメタクリレート板またはポリエステルフィルムなどが挙げられる。また、光学的に透明な保護膜としては、ポリビニルアルコール、ポリエチレングレフタレート、ポリオレフィン、ポリ塩化ビニル、ポリ塩化ビニリデンあるいはセロファンフィルムなどが挙げられる。該ホログラム記録用感光材料が前記した透明な基材上に形成されている場合は、前記した光学的に透明な保護膜を、溶液状態での塗布、静電的な密着、押し出し機を使った積層、あるいは予め粘着剤を該保護膜に塗布したフィルムを貼り合わせることによって、該感光材上に積層することができる。一方、該ホログラム記録用感光材料が前記した透明な保護膜上に形成されている場合は、光学的に透明な基材に該感光材面側を密着せしめる方法にて貼り合わせることもできる。

【0034】次に、本発明の体積位相型ホログラムの製造方法について説明する。すなわち、前記したホログラム記録媒体を、照射光、特にHe-CdレーザーおよびArイオンレーザーなどから発振される可視レーザー光線の干渉パターンに露出する第1の工程に処するが、第1の工程の前あるいは後に、紫外線、可視光線、電子線などの活性線への露出、(および)または加熱によって処理する。該記録媒体を処理するために適した活性線の光源としては、高圧水銀灯、超高圧水銀灯、高圧キセノン灯、カーボンアーク灯、ハロゲンランプ、メタルハラ

(7)

特開平6-149142

12

イドランプ、白色灯、蛍光灯、タングステンランプの他に、He-CdレーザーやArイオンレーザーなどの紫外、可視レーザーが利用できる。これら活性線に露出する時間及び露出量は活性線源によって異なるため、最適な条件設定を行う必要がある。また、加熱処理用の熱源としては、一般的には熱伝導式オープンあるいは加熱ロールが好適に用いられる。加熱処理温度範囲は、50℃から150℃の間が好ましく、より好ましくは60℃から120℃の間である。

【0035】照射線の干渉パターンに露出する第1の工程に次いで、該記録媒体を被覆している前記保護膜を該記録媒体から剝離除去せしめた後に、該記録媒体におけるアクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)を膨潤せしめる作用を有する溶媒に浸漬する第2の工程、いわゆる膨潤工程に処する。該工程に好適に用いられる溶媒としては、ベンゼン、トルエン、キシレンなどの芳香族系有機溶媒、酢酸エチル、酢酸ブチルなどの酢酸エステル系有機溶媒、アセトン、メチルエチルケトン、シクロヘキサノンなどのケトン系有機溶媒、メタノール、エタノール、イソプロパノールなどのアルコール系有機溶媒、ジオキサン、テトラヒドロフランなどの環状エーテル系有機溶媒、ジクロロメタン、クロロホルム、テトラクロロエタンなどの塩素系有機溶媒など一般的に用いられる有機溶媒、あるいはこれらの混合溶媒を適用することができる。その場合、該ホログラム記録媒体におけるアクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)を、完全には溶解せず膨潤させる作用を有することが必要で、使用する該高分子化合物(A)の種類によって適宜選択する必要がある。該膨潤工程を完了するに必要な浸漬時間は、使用する溶媒の膨潤効率及び浸漬温度によって異なるが、室温の場合、概ね30秒から5分の間にて完了する。

【0036】前記膨潤処理工程に次いで、さらに、該記録媒体に対する溶解性及び膨潤性に乏しい溶媒に、該記録媒体を接触せしめ、前記膨潤処理工程にて膨潤した該記録媒体を収縮せしめる第3の工程、いわゆる収縮処理工程に処する。該工程に好適に用いられる溶媒の具体例としては、ペンタン、ヘキサン、ヘプタン、石油エーテルなどのn-アルカン系有機溶媒が好適に用いられるが、該記録媒体を収縮せしめる作用を有する溶媒であれば、前記した溶媒に限定されるものではない。

【0037】

【作用】本発明のホログラム記録媒体は、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビ

(8)

特開平6-149142

13

ニルモノマーとの2成分以上の共重合体である高分子化合物(A)、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)、3-ケトクマリン類(C)およびジアリールヨードニウム塩(D)の組合せを含むことを特徴とする。本発明において使用される3-ケトクマリン類(C)は、A⁺イオンレーザーあるいはHe-Cdレーザーなどの可視レーザー光源から発振される可視光を効率良く吸収し、その分光増感作用によってジアリールヨードニウム塩(D)を効率良く分解する。その結果フリーラジカルが発生し、ラジカル重合が効果的に誘起されることになり、感度特性の向上に至ったものと思われる。また、アクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)を使用することによって、化学的安定性及び耐環境特性に優れ、且つ感度特性に優れた体積位相型ホログラムを製造することが可能になったと推定される。また、放射線による干渉パターンに処する前、あるいは処した後に、紫外線、可視光線、電子線などの活性線への露出、および(または)加熱による処理を施すことによって、透明性に特に優れた体積位相型ホログラムを製造するに至ったものと推察される。

【0038】また一方では、該ホログラム記録用媒体を用いた体積位相型ホログラム記録において、該記録媒体に放射線の干渉パターン露出すると、該放射線露出部位中、干渉作用の強い部位においては、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物

(B)の重合反応が生じ、支持体としてのアクリル酸エステルまたはメタクリル酸エステルの単一重合体、またはアクリル酸エステルまたはメタクリル酸エステルとビニルモノマーとの2成分以上の共重合体である高分子化合物(A)と共に網目構造を形成し、次の膨潤処理工程にて使用される溶媒に対し不溶となる。一方、放射線露出部位中、干渉作用の弱い部位においては、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)の重合反応が生じないか、あるいは、重合度が低いため、該膨潤処理用溶媒によって該記録媒体は膨潤する。これにより両部位における密度差が形成され、その結果屈折率差を生じホログラム記録がおこなわれるものと推定されるが、この作用は、該記録媒体に対する溶解性及び膨潤性に乏しい第2の溶媒に接触せしめることによって顕著に増幅され、且つまた、該記録媒体の膜厚を膨潤処理前の膜厚に戻す作用と相まって、高い回折効率およびブレイバック波長再現性に優れた体積位相型ホログラムを提供するに至ったものと考えられる。

【0039】

【実施例】以下実施例に基づき、本発明をより詳細に説明する。以下の各例において、部は特に断わりのない限り重量部を表す。

【0040】実施例1

14

ポリメタクリル酸メチル(アルドリッチ社製、重量平均分子量71万)を100部、イソシアヌル酸エチレンオキサライド変性トリアクリレート(商品名アロニックスM-315、京亜合成化学工業(株))を70部、3,3'-カルボニルビス(7-ジエチルアミノクマリン)(化合物a)を2.5部、ジフェニルヨードニウムヘキサフルオロホスフェートを5部、ジオキサンを900部からなる感光液を100×125×3mmのガラス板上に、感光液乾燥後の膜厚が6μmとなるように3ミリアブリケータを用いて塗布し、60℃オーブン中にて20分間乾燥させた。さらに、ポリビニルアルコール(アルドリッチ社製、酸化度99%以上、重量平均分子量8万)水溶液をホログラム記録用感光膜の上に塗布し、体積位相型ホログラム記録用媒体を作成した。次いで該記録媒体を90℃の熱風オーブン中で25分間の加熱処理による予備硬化を行った。この媒体に、第1図に示す体積位相型ホログラム製造用光学系で、A⁺イオンレーザーの488nm光を用いて体積位相型ホログラム記録を施した後、キシレンに1分間浸漬し感光層を現像および膨潤処理し、ヘプタンに30秒間浸漬し収縮処理させ、体積位相型ホログラムを製造した。回折効率は、日本分光工業(株)製ART25C型分光光度計で測定した。該装置は、幅3mmのスリットを有したフォトマルチメータを、試料を中心とした半径20cmの円周上に設置できる。幅0.3mmの単色光を試料に45度の角度で入射し、試料からの回折光を検出した。正反射光以外で最も大きな値と、試料を置かず直接入射光を受光したときの値との比を回折効率とした。2mJ/cm²の露光量にて、ブレイバック波長が480nm、回折効率が70%、650nmにおける透過率が92%の体積位相型ホログラムが製造された。この体積位相型ホログラムを25℃、60%RHの環境下に180日間放置しても回折効率の低下は認められなかった。

【0041】実施例2

実施例1における加熱処理による予備硬化を、60秒間の蛍光灯(60W)への露出に変えた他は、実施例1と同様の方法にて体積位相型ホログラムの製造を行った。得られたホログラム特性を第1表にまとめて示した。

【0042】実施例3～9

実施例2における3,3'-カルボニルビス(7-ジエチルアミノクマリン)を化合物(b)～(h)の3-ケトクマリン類に変えた他は、実施例2と同様の操作で体積位相型ホログラムの作製を行なった時の結果を第1表に示した。尚、実施例8、9では、ヘリウムカドミウムレーザー441nm光を用いた。得られたホログラム特性を第1表にまとめて示した。

【0043】実施例10

実施例2におけるポリメタクリル酸メチルを、ポリメタクリル酸インボルニルに変え、他は実施例2と同様の方法で操作したときのホログラム特性結果を第2表に示し

(9)

特開平6-149142

15

16

た。

【0044】実施例11

実施例2におけるポリメタクリル酸メチルを、ポリメタクリル酸フェロセニルメチルに変え、他は実施例2と同様の方法で操作したときのホログラム特性結果を第2表に示した。尚、ポリメタクリル酸フェロセニルメチルは、C. U. Pittmanらの「Macromolecules」誌の第3巻第746頁(1970年)に記載の方法にて得る事ができる。

【0045】実施例12

実施例2におけるポリメタクリル酸メチルを、ポリメタクリル酸ベンジルに変え、他は実施例1と同様の方法で操作したときのホログラム特性結果を第2表に示した。

【0046】実施例13

実施例2におけるポリメタクリル酸メチルを、ポリアクリル酸トリメチルシリルプロピルに変え、他は実施例2と同様の方法で操作したときのホログラム特性結果を第2表に示した。

【0047】実施例14

実施例2におけるポリメタクリル酸メチルを、ポリメタクリル酸メチルとスチレンの共重合体(モル比で7:3)に変え、他は実施例2と同様の方法で操作したときのホログラム特性結果を第1表に示した。

【0048】本発明における効果を明らかにするため *

*に、比較例によってさらに説明する。

【0049】比較例1

実施例1において、該記録媒体をArイオンレーザーの干渉パターンに露出しただけでは体積位相型ホログラムを製造することはできなかった。

【0050】比較例2

実施例2において、紫外灯による予備硬化処理を施さなかった他は、実施例2と同様の方法によって体積位相型ホログラムの製造を行うと、露光エネルギーが10mJ/cm²で、回折効率が70%、ブレイバック波長が480nmの体積位相型ホログラムを製造することができたが、未露光部の650nmにおける透過率が0%と、実施例2に比べ劣っていた。

【0051】比較例3

実施例2におけるメタクリル酸メチルをポリ-N-ビニルピロリドン、また現像用膨潤溶媒を酢酸エチルに変えた以外は実施例2と同様に操作して、ホログラム記録を行なった。露光量10mJ/cm²で、回折効率60%の体積位相型ホログラムの製造が可能であったが、ポリ-N-ビニルピロリドンが水溶性であるために、一日放置後、ホログラムの回折効率は10%に低下した。

【0052】

【表1】

実施例	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	ブレイバック 波長(nm)	透過率 (%)	保存性 (日)
1	488	2	70	480	92	>180
2	488	2	70	480	92	>180
3	488	4	65	480	92	>180
4	488	2	70	480	92	>180
5	488	2	70	490	92	>180
6	488	5	70	483	92	>180
7	488	3	75	480	92	>180
8	441	8	60	450	92	>180
9	441	8	65	445	92	>180

透過率は600nmにおける値

保存性は、25℃、60%RH保存下における耐久性

【0053】

【表2】

(10)

特開平6-149142

17

18

実施例	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	プレイバック 波長 (nm)	透過率 (%)	保存性 (日)
10	488	2	75	490	92	>180
11	488	10	70	485	92	>180
12	488	4	80	490	92	>180
13	488	4	65	480	92	>180
14	488	2	70	490	92	>180

透過率は600nmにおける値

保存性は、25℃、60%RH保存下における耐久性

【0054】

【発明の効果】本発明におけるホログラム記録媒体を用いた体積位相型ホログラムの製造方法により、10mJ/cm²以下の少ない露光エネルギーで、化学的安定性や耐環境特性に優れ、かつ高解像度、高回折効率、高透明性を有する体積位相型ホログラムを製造することが可能となる。

【0055】

【図面の簡単な説明】

【0056】図1は、体積位相型ホログラム製造用の二*

*光束レーザー露光装置のブロック図を示す。

【0057】

【符号の説明】

1：レーザー光源

2：ミラー

3：レンズ

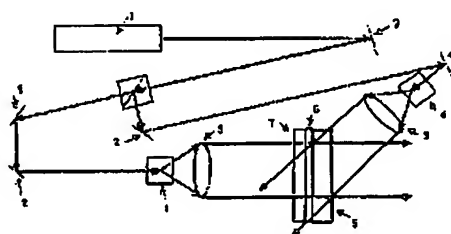
4：スペーシャルフィルター

5：基材（ガラス板）

6：ホログラム感光膜

7：保護膜（ポリビニルアルコール膜）

【図1】



PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-149142

(43)Date of publication of application : 27.05.1994

(51)Int.Cl.

G03H 1/02

G02B 1/10

(21)Application number : 04-328636

(71)Applicant : TOYO INK MFG CO LTD

(22)Date of filing : 13.11.1992

(72)Inventor : YAMAGUCHI TAKEO

TOBA YASUMASA

YASUIKE MADOKA

(54) PRODUCTION OF VOLUME PHASE TYPE HOLOGRAM

(57)Abstract:

PURPOSE: To produce the high-performance volume phase type hologram having excellent chemical stability and environmental resistance characteristic.

CONSTITUTION: 1) A photosensitive film formed by holding a photosensitive material for hologram recording contg. a combination of 4 components; 1) a single polymer of acrylate or methacrylate or a copolymer of these monomers and a vinyl monomer, 2) a compd. having a polymerizable ethylenic unsatd. bond, 3) 3-ketocumarines and 4) diaryliodonium salt with an optically transparent base material and a protective material is used as a hologram recording medium and is exposed with interference patterns. The volume phase type hologram is produced by a first stage of applying additive exposing with active rays, such as UV rays, visible rays and electron beams to the recording medium before or after the exposure or subjecting the medium to a heat treatment, a second stage of swelling the recording medium with a solvent and further a third stage of shrinking the recording medium by bringing the medium into contact with a solvent having poor solubility and swellability.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim(s)] The high molecular compound which is the copolymer of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer (A), The compound which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible (B), The sensitive material for hologram record characterized by including combination with 3-keto coumarins (C) and a diaryl iodonium salt (D) In manufacturing a volume phase mold hologram using the hologram record medium characterized by being optically inserted into a transparent protective coat with a transparent base material, and forming the film The process which consists of the 1st process which exposes this hologram record medium to the interference pattern of a radiant ray, the 2nd process processed with the solvent made to swell this record medium, and the 3rd process which this record medium is further contacted to a solvent lacking in bloating tendency, and is made to contract, The manufacture approach of the volume phase mold hologram characterized by coming to provide the process which makes this record medium process before the 1st process or to the back with the exposure to actinic rays, such as ultraviolet rays, a visible ray, and an electron ray, or (reaching) heating.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to the manufacture approach of the volume phase mold hologram which was excellent in chemical stability or environmental capability-proof, and was excellent in a sensibility property, resolution, diffraction efficiency, and especially transparency.

[0002]

[Description of the Prior Art] Conventionally, generally the sensitive material of bleaching processing silver salt and a dichromated gelatin system has been used as a hologram record medium. However, it had the trouble that each manufacture of the hologram by these hologram record media had the complicated processing for the production approach of a sensitive plate, and hologram manufacture, or a limitation was inferior to resolution in the manufactured hologram at environmental capability-proof, for example, moisture resistance, and weatherability and.

[0003] In order to solve this problem, the example using a photopolymer is known as the manufacture approach of the volume phase mold hologram equipped with the property that it should excel in environmental capability-proof, and should have holograms, such as high resolution and high diffraction efficiency. for example, in JP,62-22152,B The sensitized material which made the polyfunctional monomer which has two or more ethylene nature unsaturated bonds which are photopolymerization nature matter in the polymer which should turn into support distribute The hologram manufacture approach characterized by coming to provide the 1st process exposed to the interference pattern of a radiant ray, the 2nd process which this sensitized material is processed [process] with the 1st solvent, and makes this sensitized material swell, and the 3rd process which it processes [process] with the 2nd scarce solvent of a swelling operation, and makes this sensitized material contract is indicated. However, in the approach in this well-known reference, there was a trouble of having set at least to the part which was not exposed to the interference pattern of a radiant ray and the so-called unexposed part, and milking remarkably, in the 2nd development process. Moreover, in order to manufacture the hologram which has sufficient diffraction efficiency using the sensitized material of a publication in this well-known reference, they are 50 mJ/cm². The above exposure energy was needed and to raise further the sensibility property which turns into an important property in the extensive duplicate of a hologram, i.e., shortening of the exposure time, was desired.

[0004] On the other hand, although the photopolymerization initiator which consists of the combination of a 3-keto coumarin derivative and a diaryl iodonium salt was proposed and indicated in JP,60-88005,A (JP,3-62162,B), in the well-known reference concerned, the concrete instantiation for hologram record or the publication about the creating method was not carried out, either, and a volume phase mold hologram was not able to be created in mere use of a photopolymerization initiator given [concerned] in well-known reference.

[0005] Moreover, in a Japanese Patent Application No. No. 31590 [four to] official report, although the sensitive material for hologram record characterize by consist of combination with the compound and 3-keto coumarins which have at least one or more ethylene nature unsaturated bonds in which a

polymethyl methacrylate and a polymerization be possible, and a diaryl iodonium salt be proposed, there be a trouble that at least an unexposed part milked remarkably, in a development process.

[0006] Moreover, some manufacture approaches of a hologram using the sensitive material for hologram record and it which make a constituent a high molecular compound, the compound which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible, 3-keto coumarins, and a radical generating agent are proposed. For example, the constituent for hologram record with which the constituent for hologram record which consists of a polyvinyl carbazole or its derivative, polyfunctional monomer, a coumarin derivative, and organic peroxide becomes JP,4-13172,A from a polyvinyl carbazole, a methacrylate system compound, keto coumarin coloring matter, and an iron arene complex again is indicated by JP,2-216180,A. Since such sensitive material for hologram record was using a polyvinyl carbazole or its derivative as base resin, although they had stable and high resolution, moisture resistance, thermal resistance, and weatherability chemically, it crystalized in this development process, and they tended to milk a polyvinyl carbazole, and had the trouble that the repeatability of transparency is bad, and the fault that it was inferior in a sensibility property for the stiffness of a polyvinyl carbazole. On the other hand, although the constituent for hologram record which consists of a polyvinyl pyrrolidone, polyfunctional monomer, coumarin coloring matter, and organic peroxide was indicated in JP,2-216181,A, since a high molecular compound was water bloating tendency or water solubility, this well-known ingredient had the fault of being inferior to environmental capability-proof, such as moisture resistance and a water resisting property.

[0007]

[Problem(s) to be Solved by the Invention] This invention offers the manufacture approach of the volume phase mold hologram which was excellent in chemical stability or environmental capability-proof, and was excellent in a sensibility property, resolution, diffraction efficiency, and especially transparency.

[0008]

[Means for Solving the Problem] this invention persons result in this invention, as a result of inquiring wholeheartedly in consideration of the above many points that the above-mentioned purpose should be attained. This invention Namely, the homopolymer of acrylic ester or methacrylic ester, Or the high molecular compound which is the copolymer of two or more components of acrylic ester or methacrylic ester, and a vinyl monomer (A), The compound which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible (B), The sensitive material for hologram record characterized by including 3-keto coumarins (C) and a diaryl iodonium salt (D) In manufacturing a volume phase mold hologram using the hologram record medium characterized by being optically inserted into a transparent protective coat with a transparent base material, and forming the film The process which consists of the 1st process which exposes this hologram record medium to the interference pattern of a radiant ray, the 2nd process processed with the solvent made to swell this record medium, and the 3rd process which this record medium is further contacted to a solvent lacking in bloating tendency, and is made to contract, It is the manufacture approach of the volume phase mold hologram characterized by coming to provide the process which makes this record medium process before the 1st process or to the back with the exposure to actinic rays, such as ultraviolet rays, a visible ray, and an electron ray, or (reaching) heating.

[0009] Hereafter, this invention is explained extensively.

[0010] The high molecular compound (A) used in the hologram record medium of this invention is the copolymer of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and other vinyl monomers.

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacture approach of the volume phase mold hologram which was excellent in chemical stability or environmental capability-proof, and was excellent in a sensibility property, resolution, diffraction efficiency, and especially transparency.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] Conventionally, generally the sensitive material of bleaching processing silver salt and a dichromated gelatin system has been used as a hologram record medium. However, it had the trouble that each manufacture of the hologram by these hologram record media had the complicated processing for the production approach of a sensitive plate, and hologram manufacture, or a limitation was inferior to resolution in the manufactured hologram at environmental capability-proof, for example, moisture resistance, and weatherability and.

[0003] In order to solve this problem, the example using a photopolymer is known as the manufacture approach of the volume phase mold hologram equipped with the property that it should excel in environmental capability-proof, and should have holograms, such as high resolution and high diffraction efficiency. for example, in JP,62-22152,B The sensitized material which made the polyfunctional monomer which has two or more ethylene nature unsaturated bonds which are photopolymerization nature matter in the polymer which should turn into support distribute The hologram manufacture approach characterized by coming to provide the 1st process exposed to the interference pattern of a radiant ray, the 2nd process which this sensitized material is processed [process] with the 1st solvent, and makes this sensitized material swell, and the 3rd process which it processes [process] with the 2nd scarce solvent of a swelling operation, and makes this sensitized material contract is indicated. However, in the approach in this well-known reference, there was a trouble of having set at least to the part which was not exposed to the interference pattern of a radiant ray and the so-called unexposed part, and milking remarkably, in the 2nd development process. Moreover, in order to manufacture the hologram which has sufficient diffraction efficiency using the sensitized material of a publication in this well-known reference, they are 50 mJ/cm². The above exposure energy was needed and to raise further the sensibility property which turns into an important property in the extensive duplicate of a hologram, i.e., shortening of the exposure time, was desired.

[0004] On the other hand, although the photopolymerization initiator which consists of the combination of a 3-keto coumarin derivative and a diaryl iodonium salt was proposed and indicated in JP,60-88005,A (JP,3-62162,B), in the well-known reference concerned, the concrete instantiation for hologram record or the publication about the creating method was not carried out, either, and a volume phase mold hologram was not able to be created in mere use of a photopolymerization initiator given [concerned] in well-known reference.

[0005] Moreover, in a Japanese Patent Application No. No. 31590 [four to] official report, although the sensitive material for hologram record characterize by consist of combination with the compound and 3-keto coumarins which have at least one or more ethylene nature unsaturated bonds in which a polymethyl methacrylate and a polymerization be possible, and a diaryl iodonium salt be proposed, there be a trouble that at least an unexposed part milked remarkably, in a development process.

[0006] Moreover, some manufacture approaches of a hologram using the sensitive material for hologram record and it which make a constituent a high molecular compound, the compound which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible, 3-keto coumarins, and a radical generating agent are proposed. For example, the constituent for hologram record with

which the constituent for hologram record which consists of a polyvinyl carbazole or its derivative, polyfunctional monomer, a coumarin derivative, and organic peroxide becomes JP,4-13172,A from a polyvinyl carbazole, a methacrylate system compound, keto coumarin coloring matter, and an iron arene complex again is indicated by JP,2-216180,A. Since such sensitive material for hologram record was using a polyvinyl carbazole or its derivative as base resin, although they had stable and high resolution, moisture resistance, thermal resistance, and weatherability chemically, it crystalized in this development process, and they tended to milk a polyvinyl carbazole, and had the trouble that the repeatability of transparency is bad, and the fault that it was inferior in a sensibility property for the stiffness of a polyvinyl carbazole. On the other hand, although the constituent for hologram record which consists of a polyvinyl pyrrolidone, polyfunctional monomer, coumarin coloring matter, and organic peroxide was indicated in JP,2-216181,A, since a high molecular compound was water bloating tendency or water solubility, this well-known ingredient had the fault of being inferior to environmental capability-proof, such as moisture resistance and a water resisting property.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] By the manufacture approach of a volume phase mold hologram using the hologram record medium in this invention, it is 10 mJ/cm². It becomes possible to manufacture the volume phase mold hologram which is excellent in chemical stability or environmental capability-proof, and has high resolution, high diffraction efficiency, and high transparency with little following exposure energy.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention offers the manufacture approach of the volume phase mold hologram which was excellent in chemical stability or environmental capability-proof, and was excellent in a sensibility property, resolution, diffraction efficiency, and especially transparency.

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] this invention persons result in this invention, as a result of inquiring wholeheartedly in consideration of the above many points that the above-mentioned purpose should be attained. This invention Namely, the homopolymer of acrylic ester or methacrylic ester, Or the high molecular compound which is the copolymer of two or more components of acrylic ester or methacrylic ester, and a vinyl monomer (A), The compound which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible (B), The sensitive material for hologram record characterized by including 3-keto coumarins (C) and a diaryl iodonium salt (D) In manufacturing a volume phase mold hologram using the hologram record medium characterized by being optically inserted into a transparent protective coat with a transparent base material, and forming the film The process which consists of the 1st process which exposes this hologram record medium to the interference pattern of a radiant ray, the 2nd process processed with the solvent made to swell this record medium, and the 3rd process which this record medium is further contacted to a solvent lacking in bloating tendency, and is made to contract, It is the manufacture approach of the volume phase mold hologram characterized by coming to provide the process which makes this record medium process before the 1st process or to the back with the exposure to actinic rays, such as ultraviolet rays, a visible ray, and an electron ray, or (reaching) heating.

[0009] Hereafter, this invention is explained extensively.

[0010] The high molecular compound (A) used in the hologram record medium of this invention is the copolymer of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and other vinyl monomers. As a homopolymer of concrete acrylic ester or methacrylic ester Methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, neopentyl one, hexyl, heptyl, Octyl, nonyl, dodecyl, 2-methylbutyl, 3-methylbutyl, 2-ethyl butyl, 1, 3-dimethyl butyl, 2-ethylhexyl, 2-methyl pentyl, cyclohexyl, adamantyl, isobornyl, The acrylic acid of the shape of a chain, such as dicyclopentanil and tetrahydrofurfuryl, the shape of branching, and annular alkyl, or the polymer of a methacrylic ester monomer, Phenyl, 4-methoxycarbonyl phenyl, 4-ethoxycarbonyl phenyl, 4-butoxycarbonyl phenyl, 4-tert-buthylphenyl, Benzyl, 4-phenylethyl, 4-phenoxy diethylene glucol, 4-phenoxy tetraethylene glycol, 4-phenoxy hexa ethylene glycol, The acrylic acid containing rings, such as 4-biphenyl, or the polymer of a methacrylic ester monomer, The acrylic acid containing iron atoms, such as ferro SENIRU methyl and ferro SENIRU ethyl, or the polymer of a methacrylic ester monomer, Trifluoroethyl, tetrafluoro propyl, heptadeca fluoro DESHIRU, The acrylic acid containing halogen atoms, such as octafluoropentyl, 2, and 3-dibromopropyl, or the polymer of a methacrylic ester monomer, The acrylic acid containing silicon atoms, such as trimethoxysilylpropyl, or the polymer of methacrylic ester, The acrylic acid containing epoxy groups, such as glycidyl acrylate and glycidyl methacrylate, or the polymer of a methacrylic ester monomer, The polymer of the acrylic acid containing amino groups, such as N and N-dimethylaminoethyl, N, and N-diethylaminoethyl and t-butylamino ethyl, or a methacrylic ester monomer etc. is mentioned. These acrylic ester or a methacrylic ester monomer can be used as a copolymer of two or more components if needed.

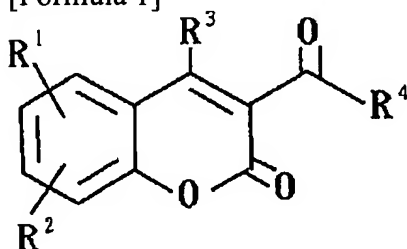
[0011] As a vinyl monomer which can be used as a copolymer of two or more components with above

mentioned acrylic ester or the above mentioned methacrylic ester monomer, a butadiene, an isoprene, acrylamide, N-butyl acrylamide, N,N-dimethylacrylamide, acrylonitrile, styrene, 4-bromostyrene, perfluoro styrene, alpha methyl styrene, vinyltoluene, vinyl acetate, a vinyl chloride, a vinylidene chloride, N-vinyl pyrrolidone, N-vinylcarbazole, vinylpyridine, a vinyl pyrrolidine, etc. are mentioned. [0012] As a compound (B) which has at least one or more ethylene nature unsaturated bonds with which the hologram record medium of this invention is presented, and in which a polymerization is possible, you may be the amount compound of macromolecules further including oligomer besides the vinyl monomer which is one organic functions, and may be such mixture. As such a compound, an acrylic acid, a methacrylic acid, an itaconic acid, A maleic acid, acrylamide, methacrylamide, diacetone acrylamide, high-boiling point vinyl monomers, such as 2-hydroxyethyl (meta) acrylate and N-vinylcarbazole, -- further An aliphatic series polyhydroxy compound, for example, ethylene glycol, a diethylene glycol, Triethylene glycol, tetraethylene glycol, neopentyl glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1, 10-Deccan diol, trimethylol propane, II or Pori (meta) acrylic ester, such as pentaerythritol, dipentaerythritol, a sorbitol, and a mannitol, An aromatic series polyhydroxy compound, for example, a hydroquinone, resorcinol, To II, such as a catechol and pyrogallol, or Pori (meta) acrylic ester, the ethylene oxide denaturation (meta) acrylate of isocyanuric acid, and a pan The polymer obtained by the macromolecule reaction of the polymer which has the functional group which has the labile like a hydroxy group or a halogenation methyl group in a side chain, and unsaturated carboxylic acid, such as an acrylic acid, a methacrylic acid, and a crotonic acid, can also be used suitably. As such a high molecular compound, a copolymer with an acrylate monomer, phenol resin, etc. are variously mentioned with the copolymer of polyvinyl alcohol, vinyl alcohol, and vinyl acetate, polyepichlorohydrin, phenoxy resin, poly chloro methyl styrene, and 2-hydroxy (meta) acrylate. Furthermore, the acrylic(meta)-ized epoxy resin, polyester acrylate oligomer, acrylic(meta)-ized urethane oligomer, acrolein-ized polyvinyl alcohol, etc. can be raised.

[0013] As 3-keto coumarins (C) of use by this invention, it is a general formula (1).

[0014] General formula (1)

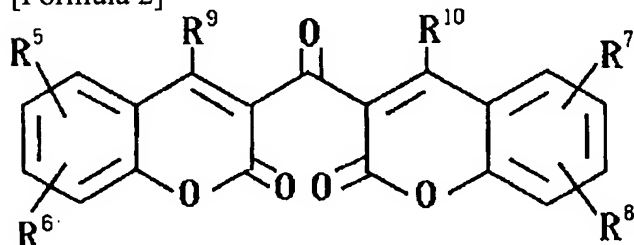
[Formula 1]



[0015] They are the 3-keto coumarins expressed with (R1 and R2 show among a formula a hydrogen atom, a halogen atom, an ARUKIKOSHI radical or a dialkylamino radical, an aryl group, or the benzene ring by which condensation was carried out, R3 shows a hydrogen atom or a cyano group, and R4 shows a low-grade alkyl group, an aryl group, heterocycle, and a styryl radical), or a general formula (2).

[0016] General formula (2)

[Formula 2]



[0017] (R5, R6, R7, and R8 among a formula) A hydrogen atom, a halogen atom, an ARUKIKOSHI radical, or a dialkylamino radical, They are at least one sort of compounds chosen as the 3rd place

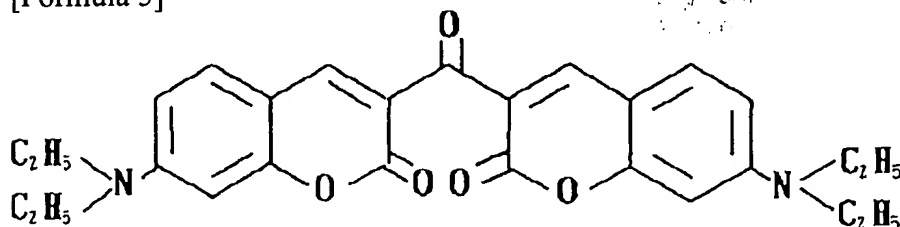
expressed from the bis-keto coumarins by which the carbonyl permutation was carried out. an aryl group or the benzene ring by which condensation was carried out -- being shown -- R9 and R10 -- a hydrogen atom or a cyano group -- being shown -- It is desirable to permute the alkoxy group or the dialkylamino radical by the benzene nucleus of a coumarin.

[0018] R1 in a general formula (1), R2 and R5 in a general formula (2), R6, R7, and R8 It sets. A fluorine, chlorine, a bromine, and an iodine atom as a halogen atom as an alkoxy group A methoxy group, an ethoxy radical, a propoxy group, an isopropanol POSHIKI radical, a butoxy radical, A butoxy radical, an iso butoxy radical, a sec-butoxy radical, a tert-butoxy radical, A benzyloxy radical etc. as a dialkylamino radical A dimethylamino radical, As an aryl group, a phenyl group, p-tolyl group, a xylyl group, a KUMENIRU radical, a naphthyl group, an anthryl radical, a phenan tolyl group, etc. are mentioned, and a diethylamino radical, a JURORIJIRU radical, etc. are mentioned for a naphthalene ring, an anthracene ring, etc. as the condensation benzene ring. Moreover, R4 in a general formula (1) It sets. As a low-grade alkyl group A methyl group, an ethyl group, a propyl group, etc. as an aryl group A phenyl group, p-tolyl group, a xylyl group, a KUMENIRU radical, a naphthyl group, an anthryl radical, As heterocycle, a benzofuran ring, a benzothiophene ring, an iso indole ring, etc. are mentioned, and a phenan tolyl group etc. is mentioned for a styryl radical, p-dimethylaminostyryl radical, p-diethylaminostyryl radical, p-methoxy styryl radical, etc. as a styryl radical.

[0019] As an example of a concrete compound expressed with a general formula (1) A 3-thieno IRUKU marine **3-(4-methoxy benzoyl) coumarin, 3-benzoyl coumarin, 3-(4-cyano benzoyl) coumarin, A 3-CHIENOIRU-7-methoxy coumarin, a 7-methoxy-3-(4-methoxy benzoyl) coumarin, A 3-benzoyl-7-methoxy coumarin, a 3-(4-cyano benzoyl)-7-methoxy coumarin, 5, 7-dimethoxy-3-thieno IRUKU marine **5, a 7-dimethoxy-3-(4-methoxy benzoyl) coumarin, The 3-benzoyl -5, 7-dimethoxy coumarin, 3-(4-cyano benzoyl)-5, 7-dimethoxy coumarin, A 7-diethylamino-3-thieno IRUKU marine **7-diethylamino-3-(4-methoxy benzoyl) coumarin, A 3-benzoyl-7-diethylamino coumarin, a 7-diethylamino-3-(4-cyano benzoyl) coumarin, A 7-diethylamino-3-(4-dimethylamino benzoyl) coumarin, A 3-(2-benzofuroyl)-7-diethylamino coumarin, a 3-cinnamoyl-7-diethylamino coumarin, A 4-cyano-3-cinnamoyl-7-diethylamino coumarin, a 3-(p-diethylamino cinnamoyl)-7-diethylamino coumarin, A 3-acetyl-7-diethylamino coumarin, a 3-carboxy-7-diethylamino coumarin, and a 3-(4-carboxy benzoyl)-7-diethylamino coumarin are mentioned. Furthermore, condensation of the ring may be carried out to the coumarin benzene ring. next, as a concrete compound expressed with a general formula (2) 3, 3'-carbonyl bisque marine **3, a 3'-carbonyl screw (7-methoxy coumarin), - carbonyl bisque marine ** 5 and 7-dimethoxy - 3 and 3 - carbonyl bisque marine **5, and '7, 7' - trimethoxy-3 and 3' -- A - carbonyl screw (5, 7-dimethoxy coumarin), and 3 and 3 '3, 3'-carbonyl screw (5, 7-diethoxy coumarin), 7-diethylamino -3, 3'-carbonyl bisque marine **7-diethylamino - 5', 7'-dimethoxy -3, 3'-carbonyl bisque marine ** A - carbonyl screw (JURORIJINO coumarin), and 3 and 3'-carbonyl screw (7-diethylamino coumarin), 3, and 3 '3, 3'-carbonyl screw (4-cyano-7-diethylamino coumarin) etc. can be raised. A compound (a) thru/or a compound (h) are shown as a typical example.

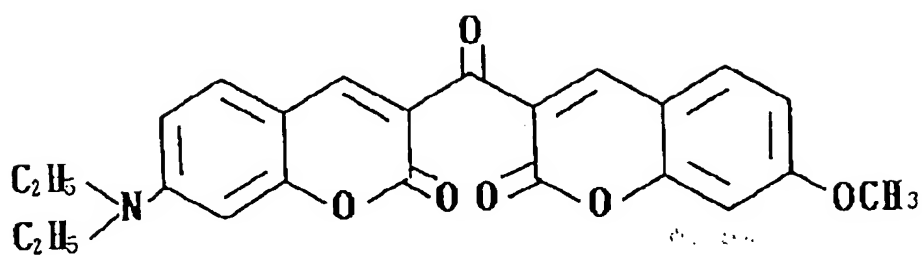
[0020] Compound (a)

[Formula 3]

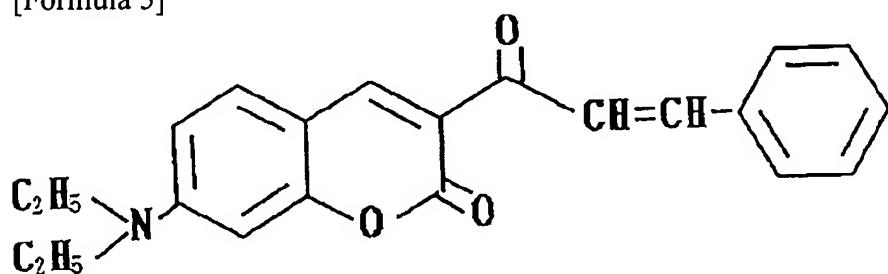


[0021] Compound (b)

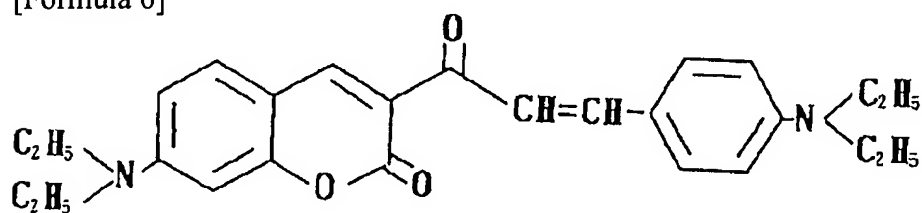
[Formula 4]



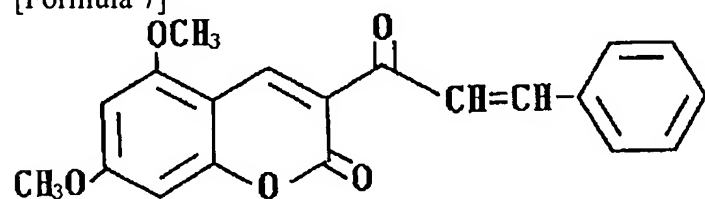
[0022] Compound (c)
[Formula 5]



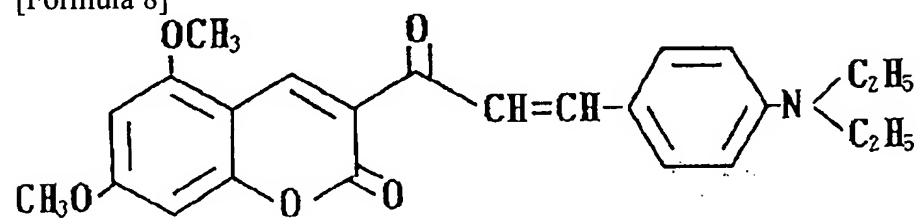
[0023] Compound (d)
[Formula 6]



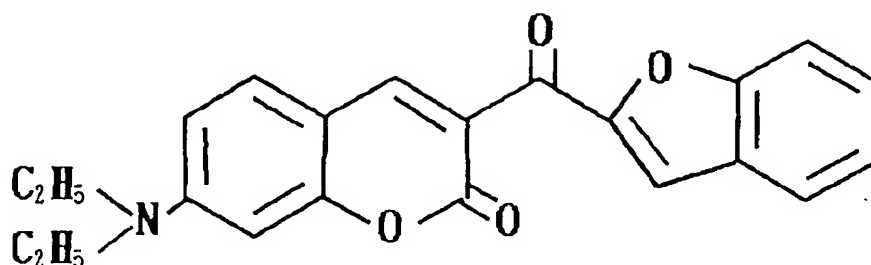
[0024] Compound (e)
[Formula 7]



[0025] Compound (f)
[Formula 8]

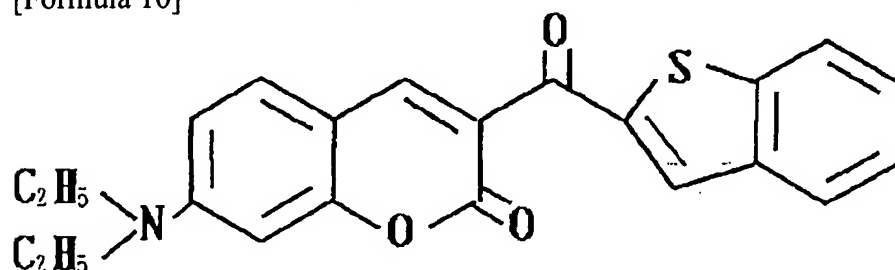


[0026] Compound (g)
[Formula 9]



[0027] Compound (h)

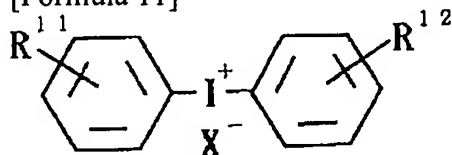
[Formula 10]



[0028] Next, the diaryl iodonium salt (D) of use by this invention is a general formula (3).

[0029] General formula (3)

[Formula 11]



the inside of a formula, and R11 and R12 -- a hydrogen atom, a low-grade alkyl group, and a lower alkoxy group -- A cyano group, a nitro group, or a halogen atom is expressed, and it is X. - Halogen ion, BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, ClO₄⁻, C₆H₅SO₃⁻, p-CH₃C₆H₄SO₃⁻, and p-CF₃C₆H₄SO₃⁻ etc. -- being shown -- the diaryl iodonium salt expressed is shown. As such a diaryl iodonium salt "Macro leakage-at-bulb KYURUSU (Macromolecules)", the 10th volume, The compound of a page [1307th] (1977) publication, for example, diphenyliodonium, JITORIRU iodonium, phenyl (p-methoxyphenyl) iodonium, Bis(m-nitrophenyl) iodonium, bis(p-tert-buthylphenyl) iodonium, Chloride, such as bis(p-cyanophenyl) iodonium, bromide, A 4 boron-fluoride salt, a 6 boron-fluoride salt, a 6 phosphorus-fluoride salt, a 6 arsenic-fluoride salt, an antimony hexafluoride salt, a perchlorate, a benzenesulfonic acid salt, a p-toluenesulfonic-acid salt, p-trifluoromethyl benzenesulfonic acid salt, etc. are illustrated.

[0030] The hologram record medium used by this invention The homopolymer of acrylic ester or methacrylic ester, Or the high molecular compound which is the copolymer of two or more components of acrylic ester or methacrylic ester, and a vinyl monomer (A), The compound which has at least one ethylene nature unsaturated bond in which a polymerization is possible (B), 3-keto coumarins (C) and a diaryl iodonium salt (D) are dissolved into a suitable solvent, and the obtained solution is optically applied in the shape of a coat on a protective coat transparent on the transparent base material up or an optical target, and it is formed. As for the thickness applied, it is desirable to make it 20 micrometers from 1 micrometer as thickness after desiccation, and its range of 4 to 10 micrometers is more desirable. Although there is no specific limit in the compounding ratio of each above-mentioned component, it is desirable to prepare the concentration of 3-keto coumarins (C) so that the permeability of the laser beam for an exposure may become 1% or more. Furthermore, various additives, for example, a plasticizer, an antioxidant, thermal polymerization inhibitor, etc. may be added if needed.

[0031] The amount occupied into the hologram record ingredient of the high molecular compound (A) which is the copolymer of two or more components of the homopolymer of acrylic ester or methacrylic

ester, acrylic ester or methacrylic ester, and a vinyl monomer is 30 - 70 % of the weight preferably ten to 90% of the weight, in order to manufacture the volume phase mold hologram which has high diffraction efficiency, high resolution, and high transparency. the (high-molecular-compound A) 100 weight section whose amount of the compound (B) used which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible is the copolymer of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer -- receiving -- the 10 - 200 weight section -- it is the 40 - 150 weight section preferably. Since maintenance of high diffraction efficiency and improvement in a sensibility property will become difficult if it deviates from the above-mentioned range, it is not desirable.

[0032] the (high-molecular-compound A) 100 weight section whose 3-keto coumarins (C) are the copolymers of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer among the photopolymerization initiators used with the hologram record medium of this invention -- receiving -- 0.1 - 30 weight section -- it is preferably used in the range of 0.5 - 15 weight section. The amount used receives a limit with the optical density of sensitization layer membrane thickness and this thickness. That is, it is desirable to use it in the range in which optical density does not exceed 2. moreover, the (high-molecular-compound A) 100 weight section whose diaryl iodonium organic boron complex (D) which is another component of a photopolymerization initiator is a copolymer of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer -- receiving -- 0.1 - 20 weight section -- it is preferably used in the range of 1 - 15 weight section.

[0033] The sensitive material for hologram record in this invention is optically used as a transparent base material and a record medium optically inserted into the transparent protective coat. As a transparent base material, a glass plate, a polycarbonate plate, a polymethylmethacrylate plate, or polyester film is mentioned optically. Moreover, as a transparent protective coat, polyvinyl alcohol, polyethylene terephthalate, polyolefine, a polyvinyl chloride, a polyvinylidene chloride, or a cellophane film is mentioned optically. When formed on the transparent base material which this sensitive material for hologram record described above, a laminating can be optically carried out on this sensitized material by sticking the above mentioned laminating using spreading in the solution condition, electrostatic adhesion, and an extruder for a transparent protective coat, or the film which applied the binder to this protective coat beforehand. On the other hand, when formed on the transparent protective coat which this sensitive material for hologram record described above, it can stick by the approach of making this sensitized material side side stick to a transparent base material optically.

[0034] Next, the manufacture approach of the volume phase mold hologram of this invention is explained. that is, although carried out on the 1st process which exposes said hologram record medium carried out to the interference pattern of the visible laser beam of light oscillated from a radiant ray especially helium-Cd laser, Ar ion laser, etc., it processes before the 1st process or to the back with the exposure to actinic rays, such as ultraviolet rays, a visible ray, and an electron ray, or (and) heating. As the light source of the actinic rays which were suitable in order to process this record medium, ultraviolet [, such as helium-Cd laser and Ar ion laser,] and the visible laser other than a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, a high-pressure xenon LGT, a carbon arc lamp, a halogen lamp, a metal halide lamp, a white LGT, a fluorescent lamp, and a tungsten lamp can be used. Since the time amount and the exposure which are exposed to these actinic rays change with sources of actinic rays, they need to perform optimal conditioning. Moreover, generally as a heat source for heat-treatment, heat circuit system oven or a heating roller is used suitably. As for a heat-treatment temperature requirement, for 50 to 150 degrees C is desirable, and it is for 60 to 120 degrees C more preferably.

[0035] After, carrying out exfoliation removal of said protective coat which has covered this record medium from this record medium subsequently to the 1st process exposed to the interference pattern of a radiant ray, it carries out on the 2nd process immersed in the solvent which has the operation which makes the high molecular compound (A) which is the copolymer of two or more components of the homopolymer of the acrylic ester in this record medium, or methacrylic ester, acrylic ester or

methacrylic ester, and a vinyl monomer swell, and the so-called swelling process. As a solvent used suitable for this process, organic solvents generally used, such as chlorine-based organic solvents, such as cyclic ether system organic solvents, such as alcoholic system organic solvents, such as ketone system organic solvents, such as acetic-ester system organic solvents, such as aromatic series system organic solvents, such as benzene, toluene, and a xylene, ethyl acetate, and butyl acetate, an acetone, a methyl ethyl ketone, and a cyclohexanone, a methanol, ethanol, and isopropanol, dioxane, and a tetrahydrofuran, dichloromethane, chloroform, and tetrachloroethane, or these mixed solvents are applicable. In that case, it is required to have the operation which it does not dissolve [operation] completely but makes the high molecular compound (A) which is the copolymer of two or more components of the homopolymer of the acrylic ester in this hologram record medium or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer swell, and it is necessary to choose suitably according to the class of this high molecular compound (A) to be used. Although immersion time amount required to complete this swelling process changes with the swelling effectiveness and immersion temperature of a solvent to be used, in the case of a room temperature, it is completed in general in 30 seconds to 5 minutes.

[0036] Subsequently to said swelling down stream processing, this record medium is made to contact a solvent still more nearly lacking in the solubility and bloating tendency over this record medium, and it carries out on the 3rd process which makes this record medium swollen in said swelling down stream processing contract, and the so-called contraction down stream processing. Although n-alkane system organic solvents, such as a pentane, a hexane, a heptane, and the petroleum ether, are used suitably, if it is the solvent which has the operation which makes this record medium contract as an example of the solvent used suitable for this process, it will not be limited to the above mentioned solvent.

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

OPERATION

[Function] The hologram record medium of this invention is characterized by including the combination of the high molecular compounds (A) which are the copolymers of two or more components of the homopolymer of acrylic ester or methacrylic ester, acrylic ester or methacrylic ester, and a vinyl monomer, (compound B) which has at least one or more ethylene nature unsaturated bonds in which polymerization is possible 3-keto coumarins (C), and a diaryl iodonium salt (D). The 3-keto coumarins (C) used in this invention absorb efficiently the light oscillated from the visible laser light sources, such as Ar ion laser or helium-Cd laser, and it decomposes a diaryl iodonium salt (D) efficiently according to the spectral sensitization operation. As a result, a free radical will be generated, induction of the radical polymerization will be carried out effectively, and it is thought that it resulted in improvement in a sensibility property. Moreover, it is guessed by using the high molecular compound (A) which is the homopolymer of acrylic ester or methacrylic ester, or the copolymer of two or more components of methacrylic ester and a vinyl monomer that it became possible to manufacture the volume phase mold hologram which was excellent in chemical stability or environmental capability-proof, and was excellent in the sensibility property. moreover, before carrying out on the interference pattern by the radiant ray, or after coping, it is imagined as a thing by having come to manufacture the volume phase mold hologram excellent in especially transparency by performing exposure to actinic rays, such as ultraviolet rays, a visible ray, and an electron ray, and (or) processing by heating.

[0038] Moreover, on the other hand, it sets to the volume phase mold hologram record which used this medium for hologram record. In the strong part of the inside of this radiant ray exposure part, and interferential action this record medium -- interference pattern exposure of a radiant ray, if it carries out The polymerization reaction of the compound (B) which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible arises. The acrylic ester as a base material, or the homopolymer of methacrylic ester, Or the network structure is formed with the high molecular compound (A) which is the copolymer of two or more components of acrylic ester or methacrylic ester, and a vinyl monomer, and it becomes insoluble to the solvent used in the following swelling down stream processing. On the other hand, among a radiant ray exposure part, in the weak part of interferential action, the polymerization reaction of the compound (B) which has at least one or more ethylene nature unsaturated bonds in which a polymerization is possible does not arise, or since polymerization degree is low, this record medium is swollen with this solvent for swelling processing. Although guessed as that to which the consistency difference in both parts is formed by this, a refractive-index difference is produced as a result, and hologram record is performed This operation is notably amplified by making the 2nd solvent lacking in the solubility and bloating tendency over this record medium contact. And having come to offer the volume phase mold hologram excellent in the operation which returns the thickness of this record medium to the thickness before swelling processing, conjointly high diffraction efficiency, and playback wavelength repeatability thinks again.

[Translation done.]

FORM PTO-1083
Mail Stop AMENDMENT
COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, VA 22313-1450

Docket No.: 331.1085
Date: July 25, 2006

In re application of: **Stefano CEVENINI et al.**
Serial No.: 10/523,562
Filed: November 9, 2005
For: **IRONING BOARD HAVING AN IRON REST**

Sir:

Transmitted herewith is a **Response to Office Action (10 pgs)** in the above-identified application.

- ☒ Also transmitted herewith are:
- ☐ Petition for extension under 37 C.F.R. 1.136
 - ☒ Return Receipt Postcard
 - ☒ Other: **One (1) Replacement Sheet of Drawings (1 pg)**
One (1) New Sheet of Drawings (1 pg)
- ☐ Check(s) in the amount of **\$00.00** is/are attached to cover:
- ☐ Filing fee for additional claims under 37 C.F.R. 1.16
 - ☐ Petition fee for extension under 37 C.F.R. 1.136
 - ☐ Other:
 - ☐ Other:
- ☒ The Assistant Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 50-0552.
- ☒ Any filing fee under 37 C.F.R. 1.16 for the presentation of additional claims which are not paid by check submitted herewith.
 - ☒ Any patent application processing fees under 37 C.F.R. 1.17.
 - ☒ Any petition fees for extension under 37 C.F.R. 1.136 which are not paid by check submitted herewith, and it is hereby requested that this be a petition for an automatic extension of time under 37 CFR 1.136.

William C. Gehris, Reg. No. 38,156

DAVIDSON, DAVIDSON & KAPPEL, LLC
485 Seventh Avenue, 14th Floor
New York, New York 10018
Tel: (212) 736-1940
Fax: (212) 736-2427

I hereby certify that the documents referred to as attached therein and/or fee are being deposited with the United States Postal Service as "first class mail" with sufficient postage in an envelope addressed to "Mail Stop: AMENDMENT Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" on July 25, 2006.

DAVIDSON, DAVIDSON & KAPPEL, LLC

BY: _____
Jennifer L. O'Connell

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

EXAMPLE

[Example] Based on an example, this invention is explained more to a detail below. In each following example, especially, the section expresses the weight section, as long as there is no notice.

[0040] Example 1 polymethyl methacrylate (the Aldrich make, weight average molecular weight 710,000) The 100 sections, An isocyanuric acid ethyleneoxide denaturation thoria chestnut rate (trade name ARONIKKUSU M-315 and Toagosei Chemical industry) The 70 sections, A 3 and 3'-carbonyl screw (7-diethylamino coumarin) (compound a) The 2.5 sections, The sensitization liquid which consists the five sections and dioxane of the 900 sections in diphenyliodonium hexafluorophosphate on a 100x125x3mm glass plate It applied using the 3-mil applicator so that the thickness after sensitization liquid desiccation might be set to 6 micrometers, and it was made to dry for 20 minutes in 60-degree-C oven. Furthermore, the polyvinyl alcohol (Aldrich make, 99% [of saponification degrees] or more, weight average molecular weight 80,000) water solution was applied on the film for hologram record, and the medium for volume phase mold hologram record was created. Subsequently, precure according this record medium to the heat-treatment for 25 minutes was performed in 90-degree C hot blast oven. By the optical system for volume phase mold hologram manufacture shown in Fig. 1, after giving volume phase mold hologram record using 488nm light of Ar ion laser, it was immersed in the xylene for 1 minute, and developed negatives and processed [swelling] the sensitization layer, and it is immersed in a heptane for 30 seconds, this medium was made to carry out contraction processing, and the volume phase mold type hologram was manufactured to it. Diffraction efficiency was measured with the ART25C mold spectrophotometer made from Jasco Industry. This equipment can install a photograph multimeter with a slit with a width of face of 3mm on a periphery with a radius [centering on a sample] of 20cm. Incidence of the homogeneous light with a width of face of 0.3mm was carried out to the sample at the include angle of 45 degrees, and the diffracted light from a sample was detected. The ratio of the biggest value except specular reflection light and the value when not placing a sample but receiving direct incident light was made into diffraction efficiency. 2 mJ/cm² With light exposure, the volume phase mold hologram whose permeability [in / playback wavelength and / in diffraction efficiency / 650nm] is 92% was manufactured 70%. [480nm] Even if it left this volume phase mold hologram for 180 days under the environment of 25 degrees C and 60%RH, the decline in diffraction efficiency was not accepted.

[0041] The precure by the heat-treatment in example 2 example 1 was changed into exposure to the fluorescent lamp for 60 seconds (60W), and also the volume phase mold hologram was manufactured by the same approach as an example 1. The acquired hologram property was collectively shown in the 1st table.

[0042] The result when changing 3 in three to example 9 example 2 and a 3'-carbonyl screw (7-diethylamino coumarin) into the 3-keto coumarins of compound (b) - (h), and also producing a volume phase mold hologram by the same actuation as an example 2 was shown in the 1st table. In addition, in the examples 8 and 9, helium cadmium laser 441nm light was used. The acquired hologram property was collectively shown in the 1st table.

[0043] Changing the polymethyl methacrylate in example 10 example 2 into polymethacrylic acid

isobornyl, others showed the hologram property result when operating it by the same approach as an example 2 in the 2nd table.

[0044] Changing the polymethyl methacrylate in example 11 example 2 into polymethacrylic acid ferro SENIRU methyl, others showed the hologram property result when operating it by the same approach as an example 2 in the 2nd table. In addition, polymethacrylic acid ferro SENIRU methyl can be obtained by the approach of a publication with a page [746th] (1970) of volume [3rd] of "Macromolecules" of C.U.Pittman and others.

[0045] Changing the polymethyl methacrylate in example 12 example 2 into polymethacrylic acid benzyl, others showed the hologram property result when operating it by the same approach as an example 1 in the 2nd table.

[0046] Changing the polymethyl methacrylate in example 13 example 2 into polyacrylic acid trimethoxysilylpropyl, others showed the hologram property result when operating it by the same approach as an example 2 in the 2nd table.

[0047] Changing the polymethyl methacrylate in example 14 example 2 into the copolymer (it is 7:3 at a mole ratio) of a polymethyl methacrylate and styrene, others showed the hologram property result when operating it by the same approach as an example 2 in the 1st table.

[0048] In order to clarify effectiveness in this invention, the example of a comparison explains further.

[0049] In example of comparison 1 example 1, a volume phase mold hologram was not able to be manufactured only by exposing this record medium to the interference pattern of Ar ion laser.

[0050] When precure processing by the fluorescent lamp was not performed and also a volume phase mold hologram is manufactured by the same approach as an example 2 in example of comparison 2 example 2, exposure energy is 10 mJ/cm². Although the volume phase mold hologram whose diffraction efficiency is 70% and whose playback wavelength is 480nm was able to be manufactured, the permeability in 650nm of an unexposed part was inferior compared with 0% and an example 2.

[0051] The methyl methacrylate in example of comparison 3 example 2 was operated like the example 2 except having changed Polly N-vinyl pyrrolidone and the swelling solvent for development into ethyl acetate, and hologram record was performed. Light exposure 10 mJ/cm² Although manufacture of the volume phase mold hologram of 60% of diffraction efficiency was possible, since Polly N-vinyl pyrrolidone was water solubility, the diffraction efficiency of a hologram fell to 10% after day neglect.

[0052]

[Table 1]

実施例	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	プレイバック 波長 (nm)	透過率 (%)	保存性 (日)
1	488	2	70	480	92	>180
2	488	2	70	480	92	>180
3	488	4	65	480	92	>180
4	488	2	70	480	92	>180
5	488	2	70	490	92	>180
6	488	5	70	483	92	>180
7	488	3	75	480	92	>180
8	441	8	60	450	92	>180
9	441	8	65	445	92	>180

透過率は600nmにおける値

保存性は、25℃、60%RH保存下における耐久性

[0053]

[Table 2]

実施例	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	プレイバック 波長 (nm)	透過率 (%)	保存性 (日)
10	488	2	75	490	92	>180
11	488	10	70	485	92	>180
12	488	4	80	490	92	>180
13	488	4	65	480	92	>180
14	488	2	70	490	92	>180

透過率は600nmにおける値

保存性は、25℃、60%RH保存下における耐久性

[Translation done.]

*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[0056] Drawing 1 shows the block diagram of the 2 flux-of-light laser aligner for volume phase mold hologram manufacture.

[0057]

[Description of Notations]

- 1: Laser light source
- 2: Mirror
- 3: Lens
- 4: Spatial filter
- 5: Base material (glass plate)
- 6: Hologram film
- 7: Protective coat (polyvinyl alcohol film)

[Translation done.]

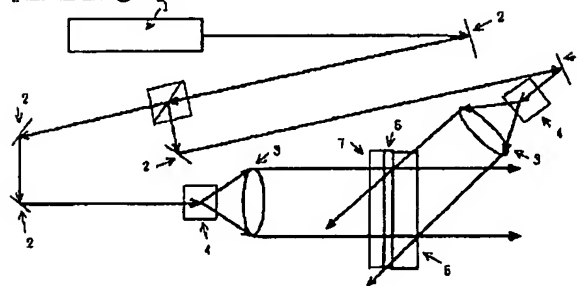
*** NOTICES ***

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]